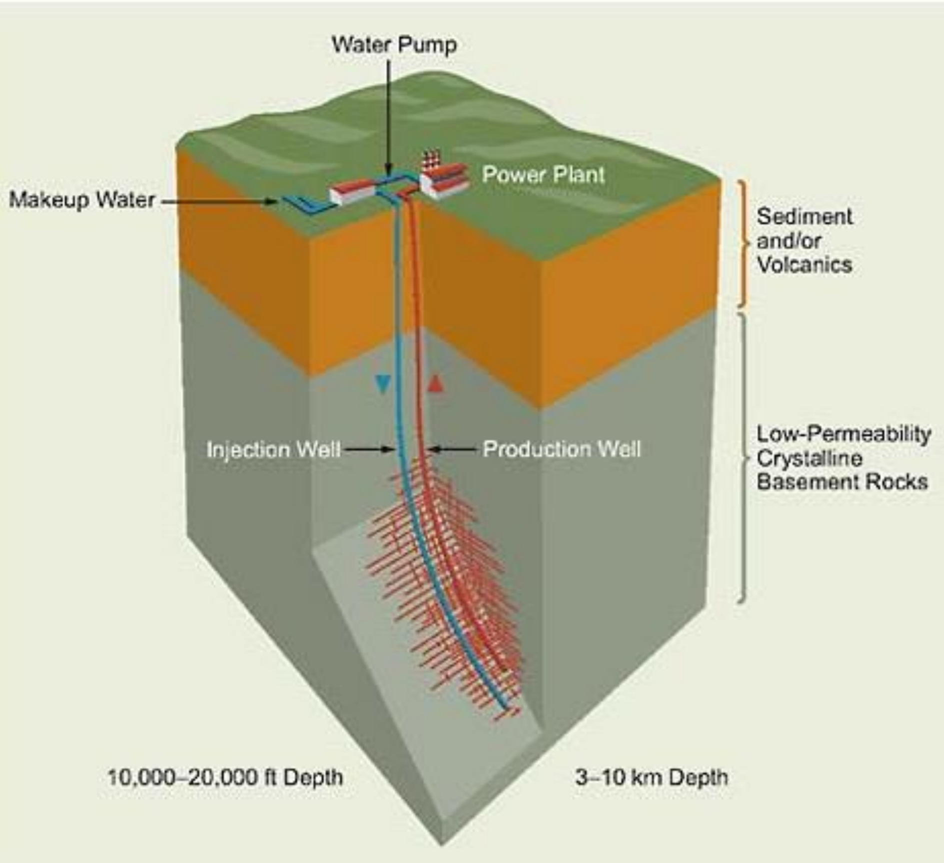
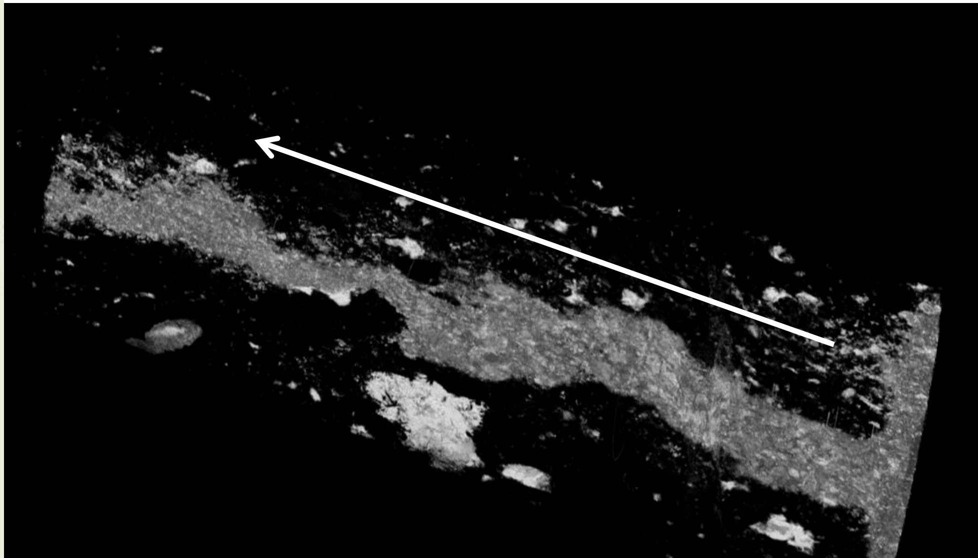


Impact of mineral reactions on shear zone permeability is uncertain at EGS conditions because key rate reactions are unknown



Increased fracture permeability after reaction with CO_2-brine at 200° C (Smith et al, 2013)

The Viability of Sustainable, Self-Propping Shear Zones in Enhanced Geothermal Systems: Measurement of Reaction Rates at Elevated Temperatures

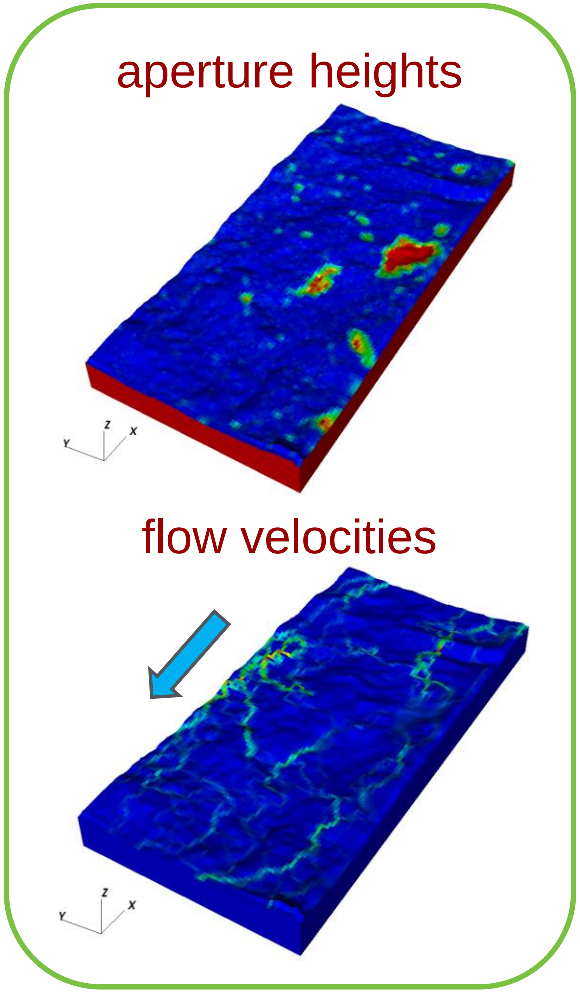
Project Officer: Elisabet Metcalf; Total Project Funding: $900,000

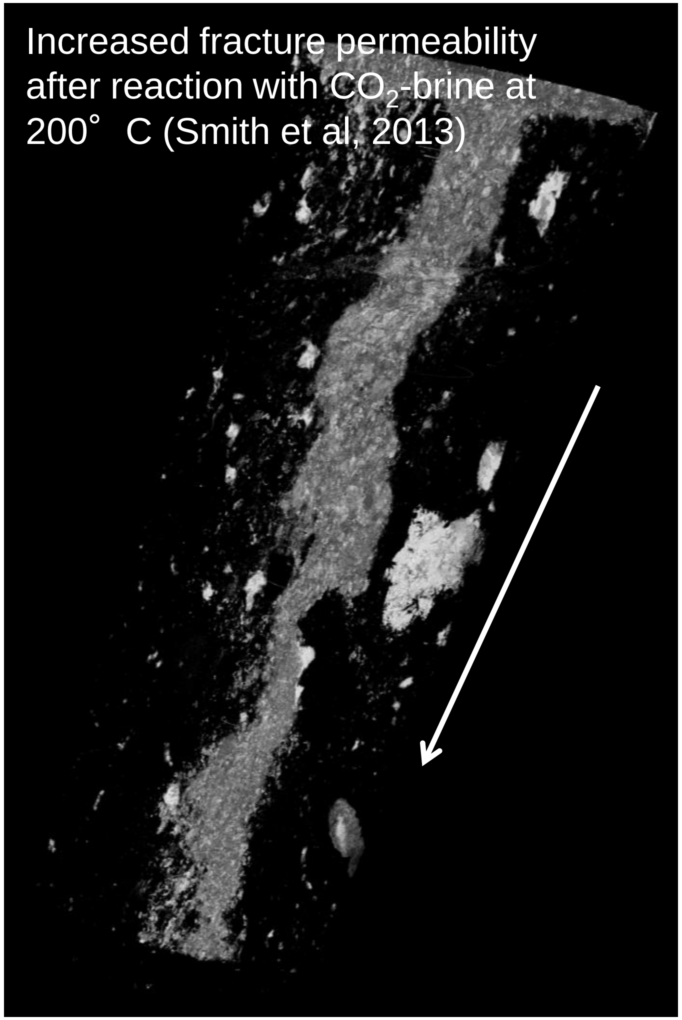
April 3, 2015

Susan Carroll
Lawrence Livermore National Laboratory

Track 3 - EGS1

- *GTO Need: Kinetic data are critical to designing and optimizing shear zone permeability for EGS systems.*

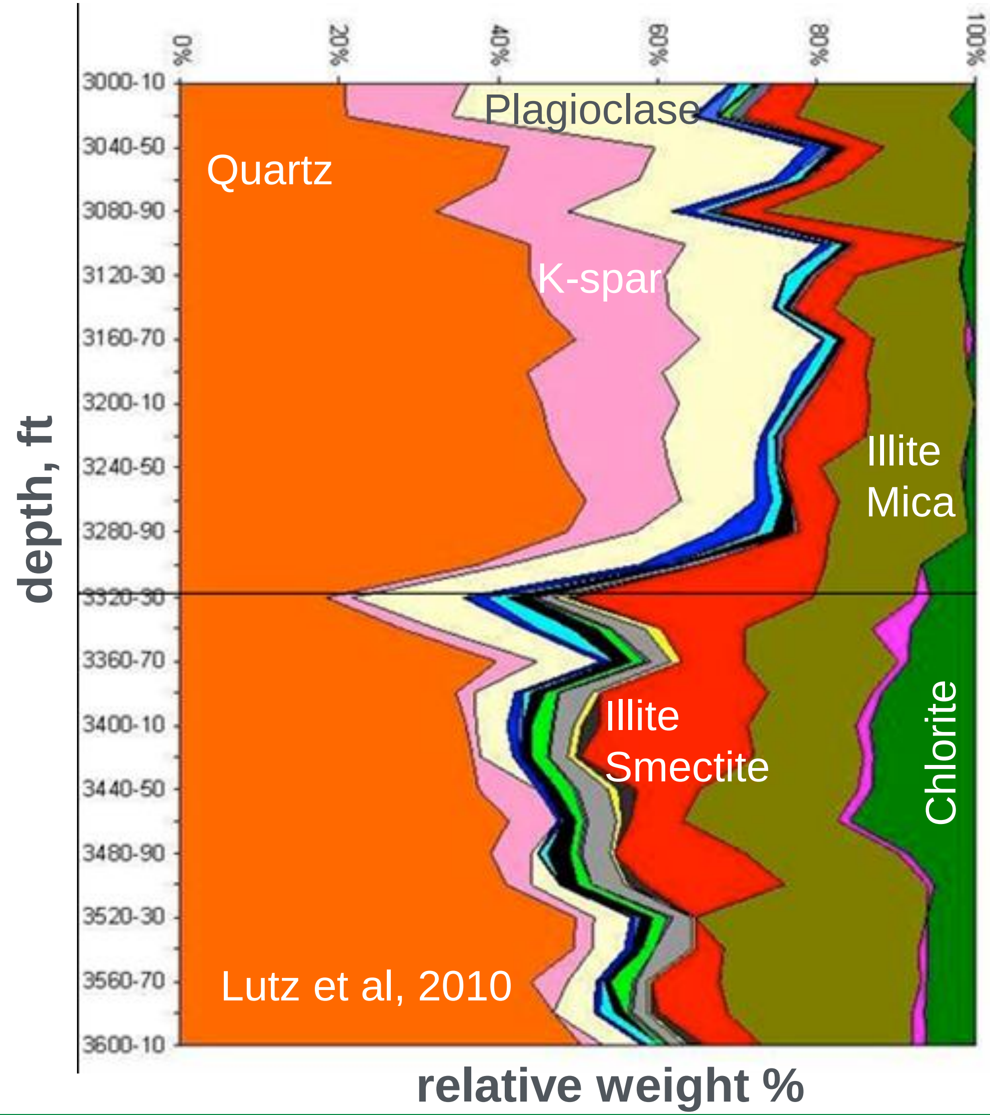




Relevance/Impact of Research

- **Kinetic Knowledge Gap Objective**
  - Expand geochemical kinetic database for fracture minerals identified in EGS shear stimulation zones to 300° C.
- **Current Technology Baseline Specifications**
  - Current kinetic data and rate equations are lacking for many shear zone minerals at EGS temperatures and are rare even to 100° C.

Shear Zone Minerals at Desert Peak



GTO Goal: Secure the Future with Enhanced Geothermal Systems

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- Results will allow chemical affects to be included in modeling, allow realistic estimates of risk from chemical reactions, and assist in designing economically viable EGS systems.

- Rate equation
  - Temperature
  - pH
  - Solution chemistry
  - Surface area

$$R\ (mol\ s^{-1}) = S\left(\left[A_A \cdot e^{-E_A/\mathrm{RT}} \cdot a_{H^+}^{n}\right] + \left[A_N \cdot e^{-E_N/\mathrm{RT}}\right] + \left[A_B \cdot e^{-E_B/\mathrm{RT}} \cdot a_{OH^-}^{m}\right]\right) \cdot f(\Delta G_r)$$

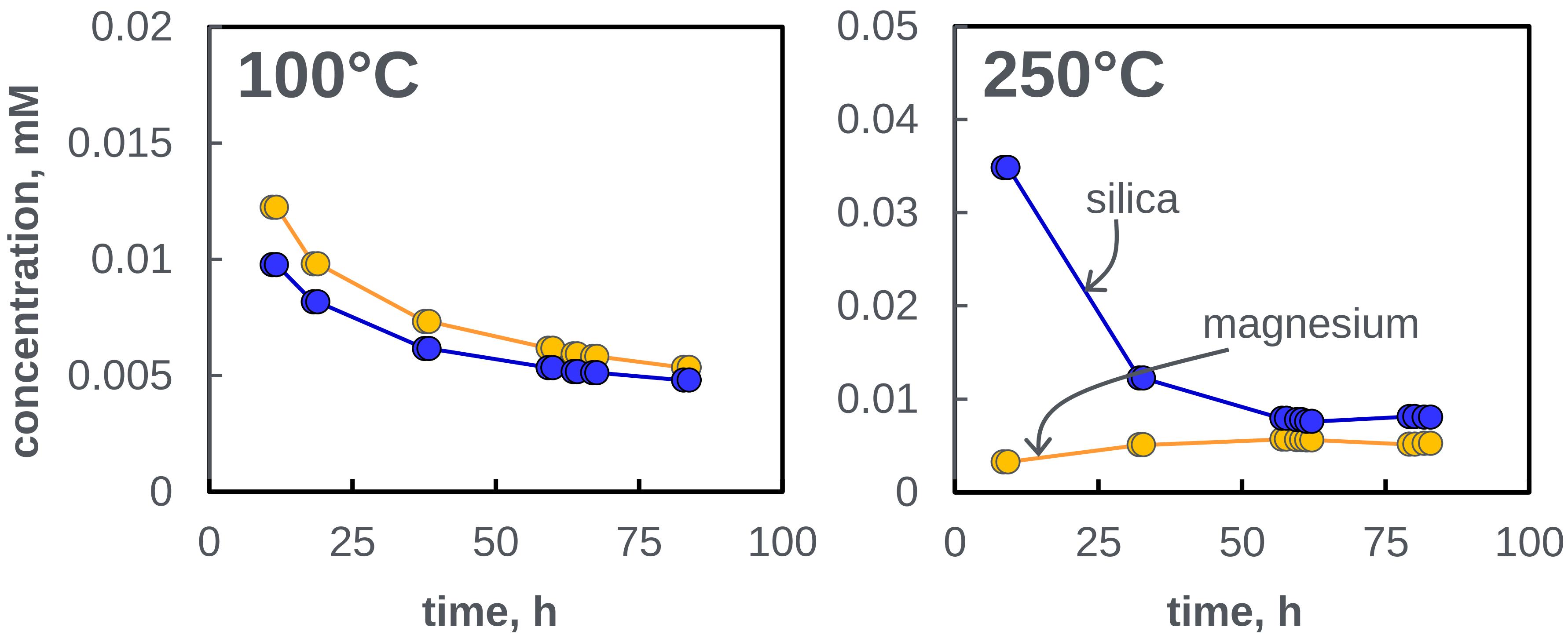
  - Collaboration with Tim Kneafsey at LBNL: **Sustainability of Shear-Induced Permeability for EGS Reservoirs – A Laboratory Study**

Scientific/Technical Tasks

- Detailed characterization of solids before and after reaction
  - TEM/SEM/XRD/BET
- Measure dissolution rates for shear zone minerals in mixed flow reactors
  - chlorite, illite, and biotite
  - pH 3 – 10
  - 100 - 300° C
  - $f(\Delta G_r)$
    - Desert Peak, Raft River, Bradys Hot Spring (~200° C)
    - Newberry (200-300° C)
- Derive dissolution rate equations to be used in reactive-transport simulations

$$R\ (mol\ s^{-1}) = S\left(\begin{array}{c}\left[A_A \cdot e^{-E_A/\mathrm{RT}} \cdot a_{H^+}^{n}\right] + \left[A_N \cdot e^{-E_N/\mathrm{RT}}\right] \\ +\left[A_B \cdot e^{-E_B/\mathrm{RT}} \cdot a_{OH^-}^{m}\right]\end{array}\right) \cdot f(\Delta G_r)$$

- Rate ~ Δ [solution composition] x flow rate / surface area



Chlorite Dissolution

$(Mg_{4.29}Al_{1.48}Fe_{0.10})(Al_{1.22}Si_{2.78})O_{10}(OH)_8$

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- Rate equation optimized for 100 to 275° C – 52 experiments
- Rate equation optimized for 25 to 275° C – 161 experiments
- Observations
  - Rates have a slight dependence of temperature
    - Not due to aqueous diffusion – rates would be 100 to 1000 times faster than measured
  - Rates have a weak dependence on alkaline pH
  - Rates are incongruent – evidence for $Mg(OH)_2$ and $Al(OH)_3$ precipitation
  - Rates do not appear to be impacted by solution saturation even though equilibrium is approached at alkaline pH

Chlorite: High Temperature Rate Equation (100 to 275° C)

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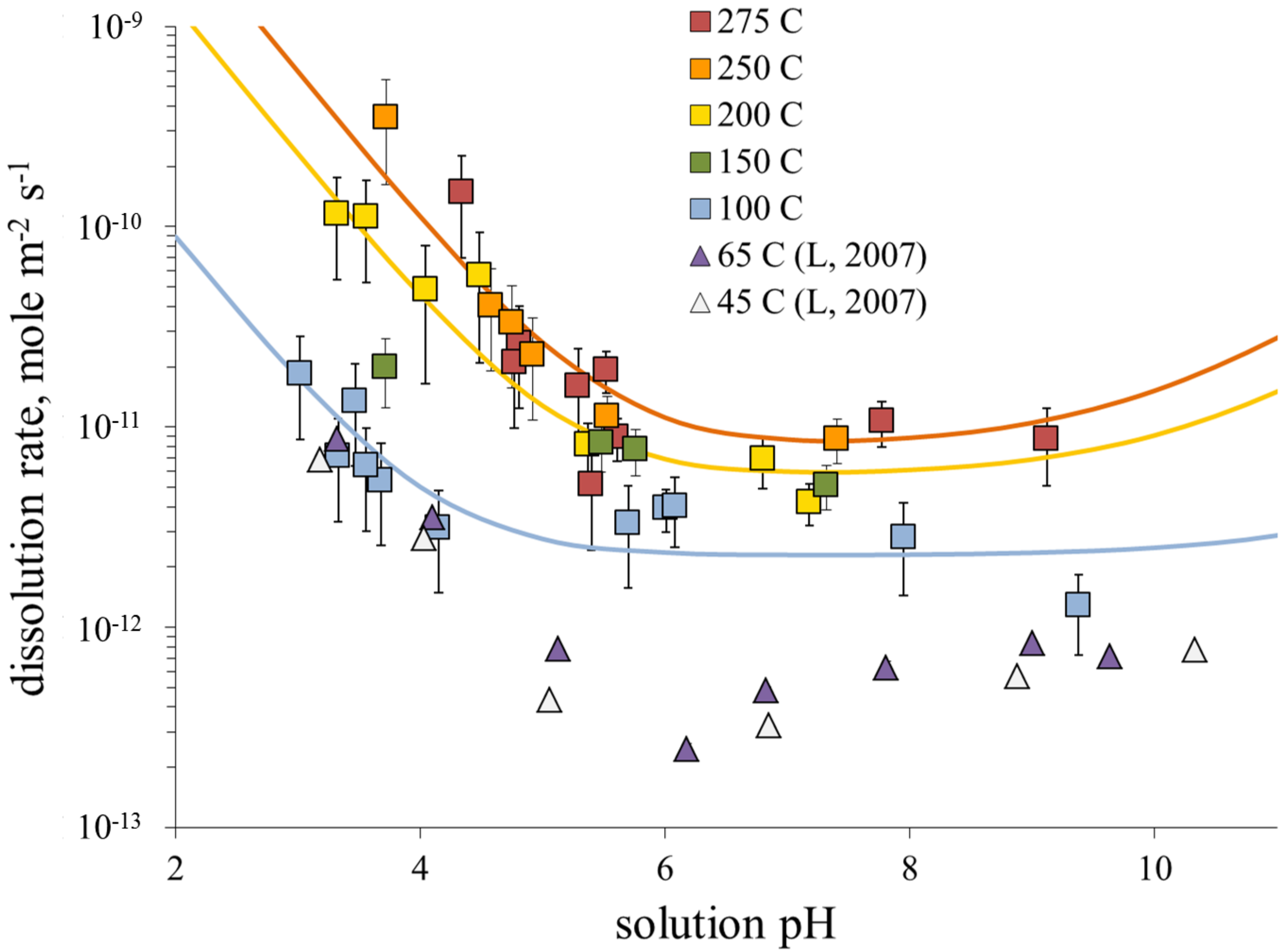
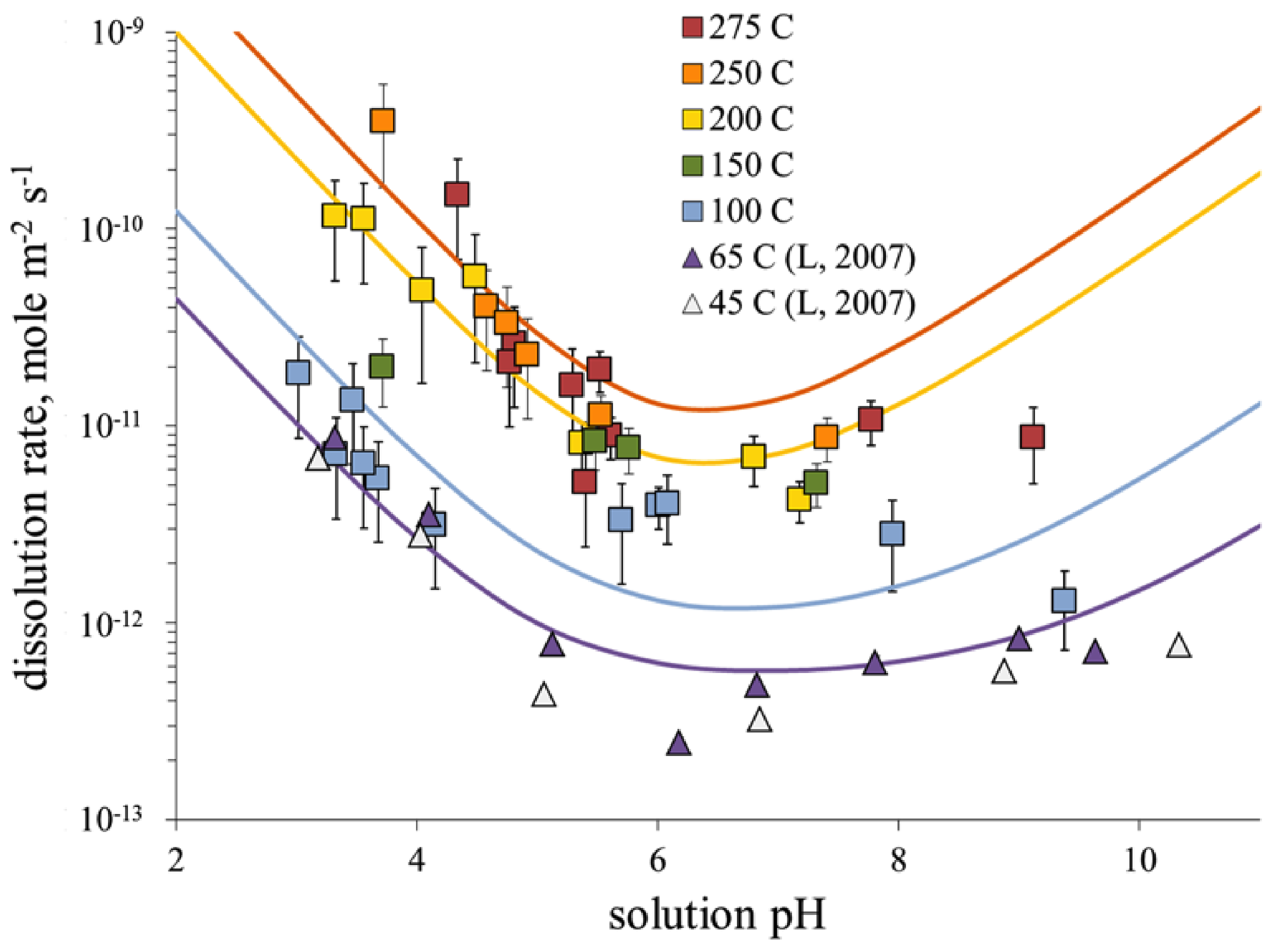


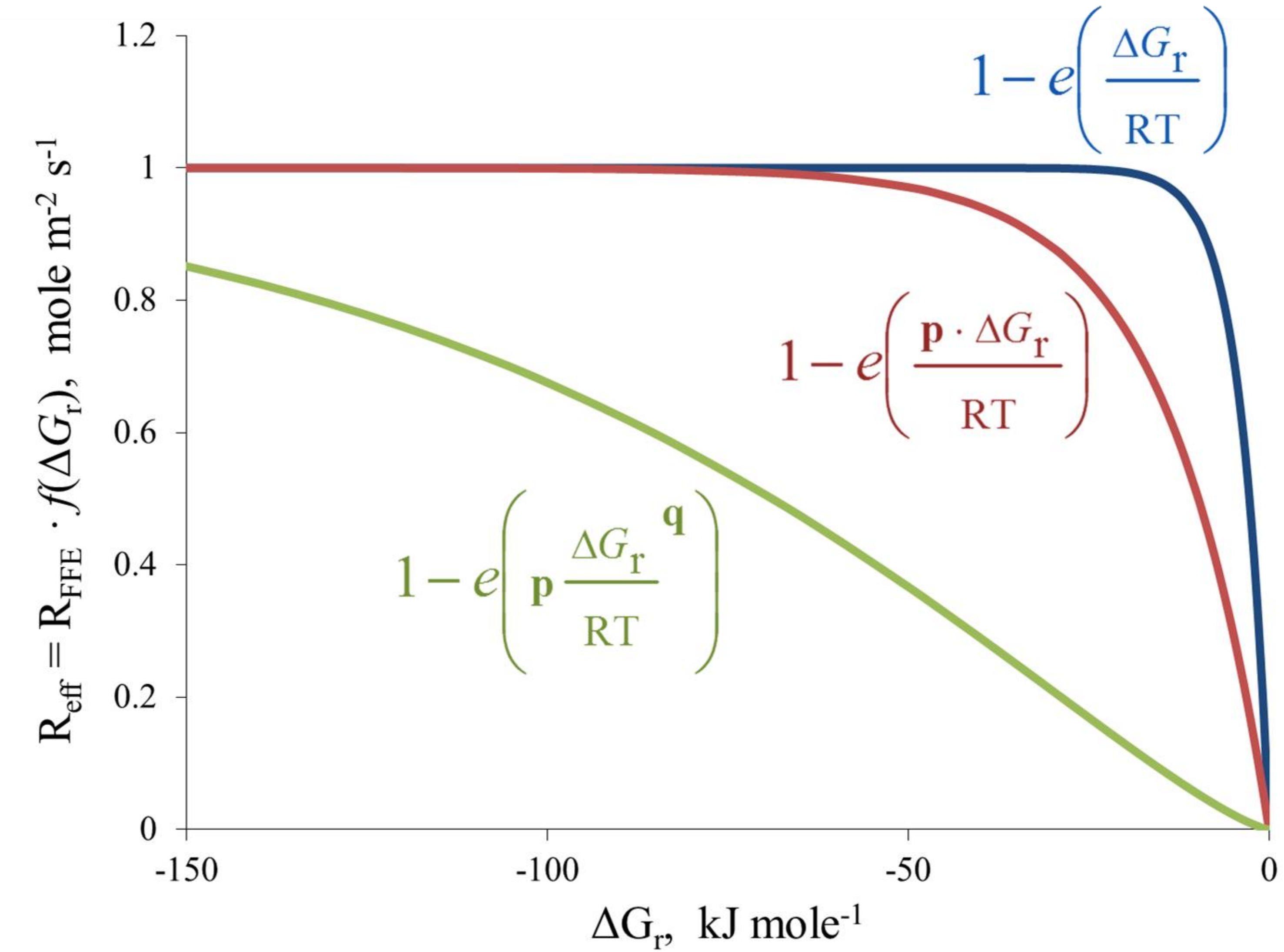
$$R(mole\ s^{-1}) = S\left(\left[9\cdot 10^{-4}\cdot e^{-39.4/\mathrm{R\cdot T}}\cdot a_{H^+}^{0.75}\right] + \left[1.6\cdot 10^{-10}\cdot e^{-13.2/\mathrm{R\cdot T}}\right] + \left[1\cdot 10^{-8}\cdot e^{-26.3/\mathrm{R\cdot T}}\cdot a_{OH^-}^{0.43}\right]\right)$$

Chlorite: Single rate equation from 25 to 275° C



$$R\ (mole\ s^{-1}) = S\left(\left[5 \cdot 10^{-5} \cdot e^{-30.8/_{\mathrm{R \cdot T}}} \cdot a_{H^+}^{0.65}\right] + \left[3 \cdot 10^{-10} \cdot e^{-18.0/_{\mathrm{R \cdot T}}}\right] + \left[2 \cdot 10^{-7} \cdot e^{-26.3/_{\mathrm{R \cdot T}}} \cdot a_{OH^-}^{0.43}\right]\right)$$

Theoretical $f(\Delta G_r)$ terms slows rates only when the solution is very close to equilibrium



Illite Dissolution

$K_{1.55}(Na_{0.04},Ca_{0.02})Al_{2.90}(Fe_{0.70},Mg_{0.54},Ti_{0.05})Si_{6.75}Al_{1.25}O_{20}(OH)_4$

- Rate equation is still under development
  - 23 experiments from 100 to 275° C
  - 47 experiments from 25 to 275° C

- Observations
  - Measured rates depend on illite dissolution and precipitation of a K-Al-silicate
  - Need to identify secondary phase (TEM)
  - Extract dissolution and precipitation reactions from the measurements

Illite: Mixed dependence on pH above 100° C

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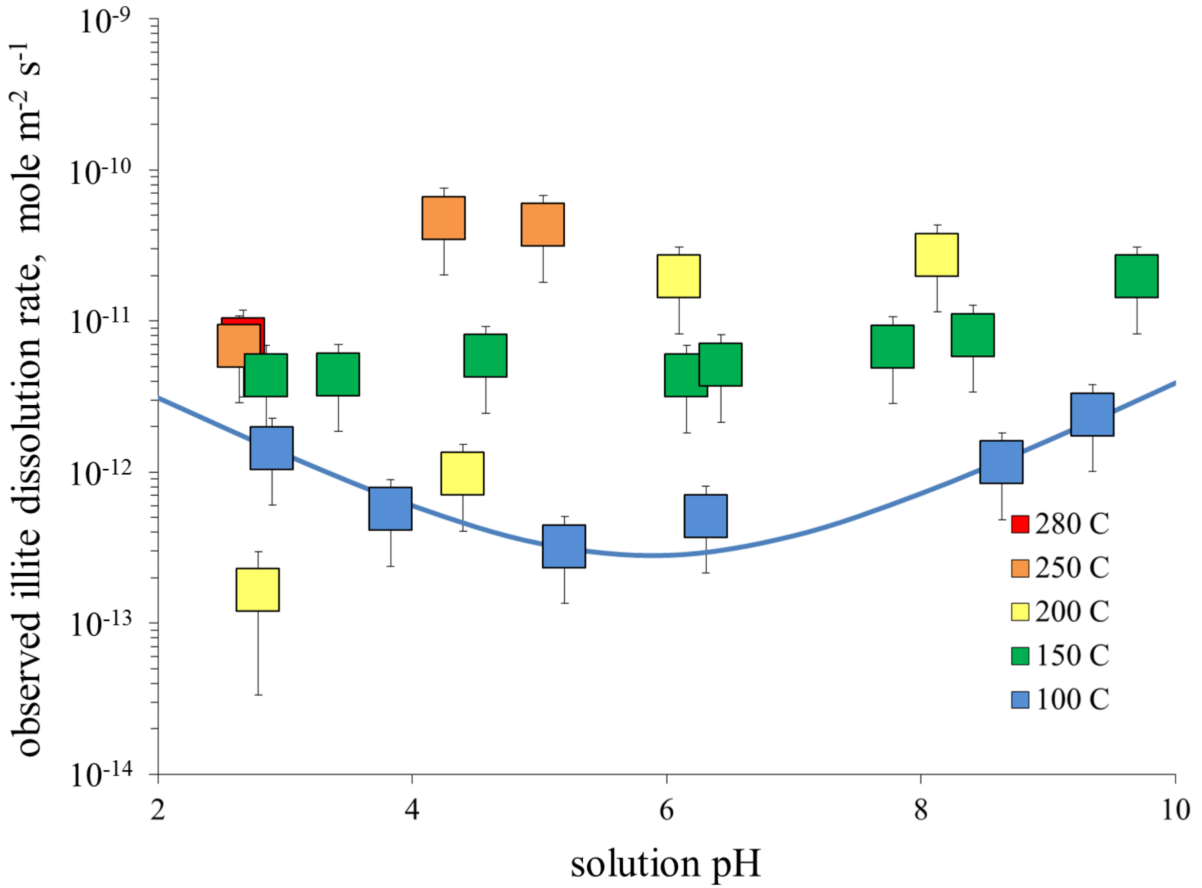
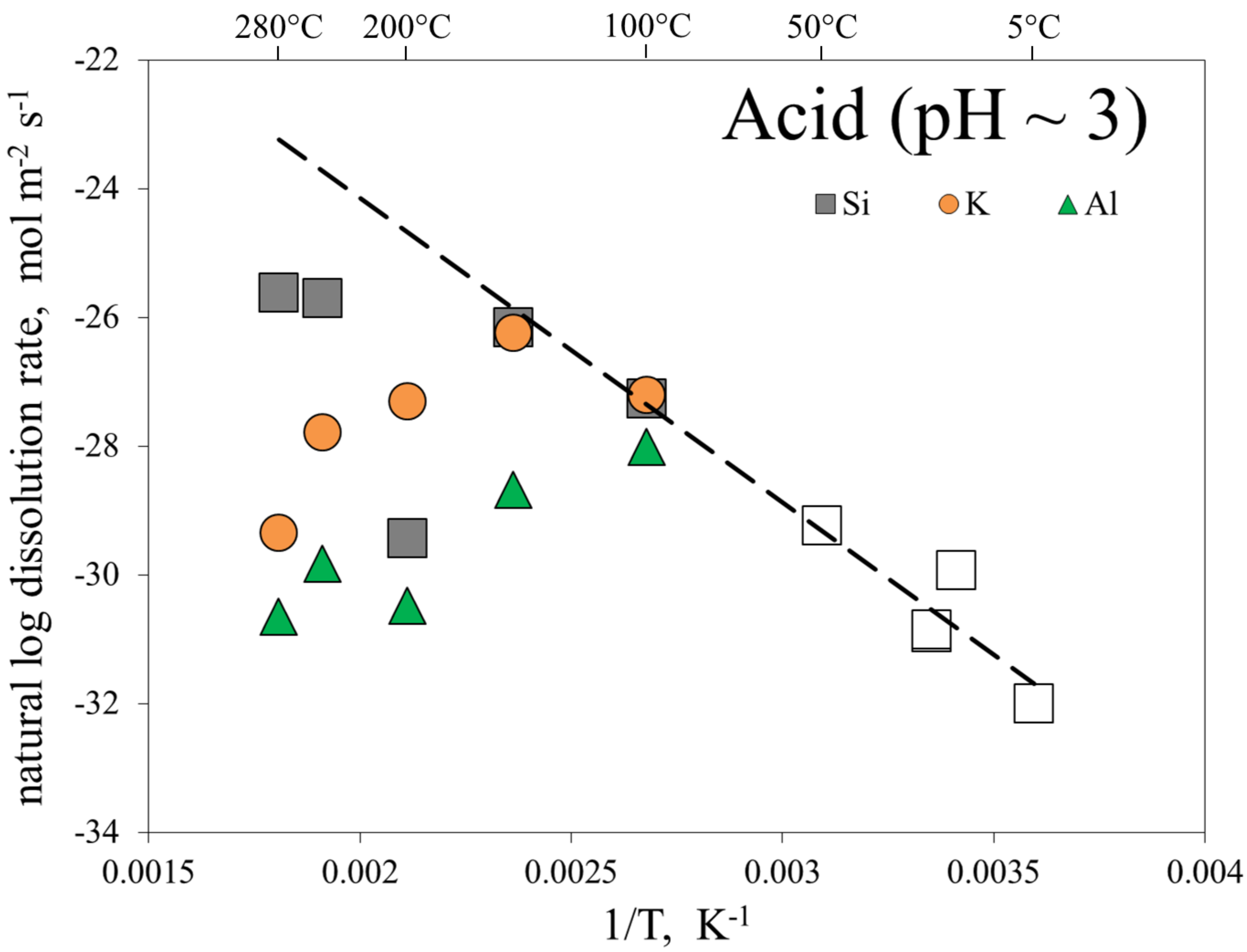


$$R_{illite}\ (mole\ s^{-1}) = S\left(\left[1\cdot 10^{-5}\cdot e^{-40.9/\mathrm{R\cdot T}}\cdot a_{H^+}^{0.40}\right] + \left[7\cdot 10^{-11}\cdot e^{-20.0/\mathrm{R\cdot T}}\right] + \left[1\cdot 10^{-4}\cdot e^{-46.6/\mathrm{R\cdot T}}\cdot a_{OH^-}^{0.40}\right]\right)$$

Illite: High Al to Si ratios lead to K-Al-silicates precipitation at higher temperature



Summary: Rock-water interactions have the potential to alter shear zone permeability

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- Chlorite, illite, and biotite are key fracture filling minerals in EGS shear zones
- Measured rates and derived dissolution equations for chlorite and illite from 100 to 280° C that can be used to assess the role of geochemistry for EGS permeability using reactive transport codes
- Biotite experiments are on-going
- Additional data gaps for pure minerals and mixed clays
  - Smectite, Epidote, Plagioclase
  - Muscovite/Illite/Smectite

Future directions

- To Complete Project
  - Refine illite dissolution equation
  - Finish biotite experiments and derive rate equation
  - Submit and update data and rate equations to Geothermal Data Repository

- Future Project
  - Assess the affect of coupled mineral dissolution and precipitation on site specific cores using a Monte Carlo approach to capture chemical uncertainty
  - Continuation of collaboration with Tim Kneafsey at LBNL

Accomplishments, Results and Progress

Status

- FY15 will focus on illite and biotite dissolution rates. We will try and do some experiments with smectite if we have time/resources.
- Major technical challenge: Deriving rates from minerals that exhibited precipitation of a secondary phase

Deliverable

- Final report documenting updated EGS mineral kinetic database by 9/30/15

Original Planned FY15 Milestones	Date Planned	Date Completed
Finish measuring illite dissolution rates	March 31, 2015	March 15, 2015
Refine illite dissolution equation	March 31, 2015	Revised April 30, 2015
Present illite results at Stanford Geothermal meeting	January 2015	January 2015
Participate in GTO Program Review	May 11, 2015	May 11, 2015
Measure biotite dissolution rates	September 30, 2015	
Derive biotite dissolution equation	September 30, 2015	